3. The density of silver phosphate is found to be 6.37.

4. It is found that silver phosphate does not adsorb a significant amount of air.

5. Nine analyses, made with four different samples, show that 1 gram of silver phosphate yields 1.34562 grams of silver bromide, whence the per cent. of silver in silver phosphate is 77.300.

Therefore,

If Ag = 107.88	P = 31.04
If Ag = 107.87	P = 31.03
If Ag = 107.86	P = 31.02

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THE SOLUBILITY OF GOLD IN NITRIC ACID.[1]

BY FREDERIC P. DEWEY.

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If there is any statement that is firmly established in general chemical literature it is that gold is not soluble in any single acid. In the literature of assaying, however, may be found various statements to the effect that, in parting gold from silver in assaying, gold may go into solution in the nitric acid used.

Makins[2] boiled a series of samples of parted gold in nitric acid of two different strengths and found an increasing loss of gold depending upon the amount of boiling, but he did not establish the purity of the acid used, nor the presence of gold in the acid after boiling. Neither did he determine the amount of silver remaining in his cornets.

In discussing the causes of loss of gold in making gold bullion assays, Rose[3] states that 8 per cent. of the loss is due to the gold going into solution in the nitric acid during parting. This statement is apparently based upon the author's own work, but no details are given to explain or sustain it.

Rickets and Miller[4] quote this statement from Rose without comment.

In his latest book Rose,[5] immediately after the general statement that gold is not perceptibly attacked by nitric acid, adds that finely divided gold is slightly soluble in boiling nitric acid, but gives no experimental data.

In speaking of the silver remaining in the gold after parting, Lodge[6] says, "If strong nitric acid (1.42 sp. gr.) is used this amount of silver may

[1] Presented by permission of the Director of the Mint.

[2] *Quarterly Journal Chemical Society*, **13**, 99 (1861).

[3] "Metallurgy of Gold," p. 479.

[4] "Notes on Assaying," p. 129.

[5] "Precious Metals," p. 14.

[6] "Notes on Assaying," p. 144.

be slightly reduced, but the gold will begin to dissolve." However, he gives no data upon the subject.

Hillebrand and Allen,[1] after reviewing various previous statements upon the subject, describe their own tests, which tended to show that parted gold was slightly soluble in nitric acid. Their results, however, are not conclusive, for, while we may assume that reasonable precautions were taken to insure the purity of the acid used, these precautions are not stated and, while the utmost care was taken to guard against loss by float gold, yet invisibly fine particles of gold may have been suspended in the acid. It would have been better if the solutions had been filtered before evaporation, and if the porcelain dishes containing the residue after evaporation had been gently heated with a few drops of aqua regia, and a small amount of strong hydrogen sulphide water added, and the solution filtered off before the dishes were wiped out with filter paper, adding the filter to the wiping paper before cupelling. Again, in testing the parting solutions for gold, no tests are given to show the freedom of the separated silver from gold.[2]

The chief difficulty militating against the certainty of the results in experimenting upon this subject lies in the minute quantities involved when only small quantities of gold are employed for the tests.

For a long time I have been engaged upon an extensive investigation into the accuracy of gold bullion assays. A preliminary paper giving the figures obtained in comparing many hundred assays was read at the Seventh International Congress of Applied Chemistry at London, May 27 to June 3, 1909, and at the Spokane meeting of the American Institute of Mining Engineers.[3] This paper will also be published in the forthcoming report of the Director of the Mint for the fiscal year ended June 30, 1909.

In following up this matter by an investigation into the conditions surrounding and affecting the accuracy of the work of making a gold bullion assay, the possible solubility of the gold in the nitric acid during parting becomes an important point. My preliminary results were so decisive that the work was somewhat extended and it was found easy enough to thoroughly demonstrate this solubility when large amounts of gold were employed and to dissolve finely divided gold in boiling nitric acid of 1.42 sp. gr. with only a small amount of gold.

A few tests made upon regular assay work will suffice here. The acid from parting nine fine gold assays was treated with a very small amount of hydrochloric acid, the precipitate filtered off and assayed, yielding 0.33 mg. of gold. To the filtrate a small amount of lead acetate was

[1] Comparison of assays, "Gold Telluride Ores," *Bull.* **253,** U. S. Geological Survey, p. 27.

[2] Prof. Hillebrand wishes me to state that the acid used by them was 1:1.

[3] *Bull. Am. Inst. Mining Eng.*, August, 1909, p. 705.

added and then sulphuric acid. The whole was evaporated to fumes, the residue filtered off and assayed, yielding 0.04 mg. of gold.

The acid from nine coin proof assays was allowed to stand several days, when it was filtered and the filter paper was assayed, yielding 0.29 mg. of gold. To the filtrate a small amount of hydrochloric acid was added and the precipitate assayed showing 0.02 mg. of gold. A second treatment with hydrochloric acid gave no gold.

The acid from nine coin proof assays was filtered when nearly cold and the filter yielded 0.26 mg. gold. On standing two days and filtering again 0.16 mg. of gold were recovered. Treatment of the second filtrate with a very slight amount of hydrochloric acid failed to give any more gold.

In our regular assay work we boil the cornets twice in 1 : 1 acid for 10 min. each time and then in 3 : 2 acid for 10 min. In the next test on nine coin proof assays the acids were kept separate. On filtering, when cool, not cold, Nos. 1 and 2 gave only questionable indications of gold while No. 3 yielded 0.02 mg. of gold. On standing $3^1/_2$ days and filtering, No. 1 gave no visible gold, No. 2 only the faintest specks, while No. 3 gave 0.14 mg. of gold. On treating the filtrate with a very slight amount of hydrochloric acid, Nos. 1 and 2 gave no gold, but No. 3 gave 0.02 mg. gold. On treating the second filtrates with a small amount of hydrogen sulphide water all three samples failed to show gold.

While these results may appear to be somewhat confused, yet they show conclusively that the acid from the parting carries gold, that, while the gold is not visible, yet some of it may be removed by filtering and that even after standing and filtering again gold may still be recovered from the filtered acid.

This state of affairs might give rise to considerable speculation as to just what the action of the acid on the gold might be, but I pass to further more elaborate and more conclusive tests.

As the amounts of gold recovered in the tests upon our regular assay work were so small I prepared some special melts of metal, approaching the composition of our regular assay buttons, but containing differing proportions of silver, and loaded the parting basket in one case to its utmost capacity. The small bars were rolled out thin, with frequent annealing, cut into strips and put into the regular cups in the basket.

The first metal contained about 20 grams of gold, 46 grams of silver, a little copper and less lead. This sample was boiled three times for ten minutes each in the dilute acid and twice in the stronger acid. A total of 1.30 mg. of gold was recovered from the fifth acid. The cornets remaining after this prolonged boiling weighed 20.61 grams and contained 22.36 mg. silver.

The nitric acid used in the tests so far described was taken from the

regular laboratory supply and, while I have no especial reason for doubting its integrity, for the next test the acids were especially prepared by treating a large conical flask of each strength with a little nitrate of silver and allowing them to stand at rest for over a week before using them.

The second metal consisted of 25.03 grams of cornet gold, 63.7 grams of silver, 0.125 gram copper and 0.075 gram lead. This sample was boiled four times in the dilute acid and three times in the stronger acid for varying lengths of time, and then given a fifteen-minute boil in the full strength of 1.42 sp. gr. acid. The acid from the last boil was colored distinctly yellow. After standing four days, the acid from the seventh boil, which was 15 minutes in 3 : 2 acid, was filtered and the filter showed 0.12 mg. of gold, while the filtrate showed 1.48 mg. of gold.

The gold was then boiled in a tall plain beaker in 1.42 acid from the laboratory stock for a full hour, producing about 500 cc. of a yellow solution, carrying gold at the rate of 77.2 mg. per liter.

The gold was then boiled in 1.42 acid from the laboratory stock for two hours producing about 600 cc. of a bright yellow solution, carrying gold at the rate of 183.3 mg. per liter.

The cornets remaining after this drastic treatment weighed 24.83 grams and carried 6.38 mg. of silver.

A third metal was prepared from 30 grams of cornet gold, 80 grams silver, 0.15 gram copper and 0.08 gram lead, but this was a little more than the platinum basket would hold. As this metal contained rather a large proportion of silver it was cautiously treated with the dilute (1 : 1) acid to remove the silver with only a small amount of disintegration of the gold. It was then boiled nearly an hour in the stronger (3 : 2) acid.

As a quicker and more certain precaution against the possible presence of chlorine in the nitric acid, the 1.42 acid next used was boiled in the beaker at about 120° for about two hours before the introduction of the gold, after which the boiling was continued for a trifle over three hours, producing nearly 700 cc. of a bright yellow solution, carrying gold at the rate of 186.4 mg. per liter.

The next test was made in the platinum parting apparatus. About 300 cc. of acid were boiled for an hour, the gold introduced, and the boiling continued for another hour. This solution contained 26.69 mg. of gold, or about 175 mg. per liter.

A final crucial test was carried out in the platinum parting apparatus with every possible precaution. I personally opened, with the utmost care, a fresh bottle of nitric acid of the J. T. Baker Chemical Company's make, bearing the following analysis:

Specific gravity.....	1.415–1.42
Nitric acid.....	69–70 per cent.
Sulphuric acid.....	None.

Hyponitrous acid.....	None
Chlorine.....	"
Iodine.....	"
Iron.....	0.0002 per cent.
Non-volatile matter.....	0.001 "

Lot No. 7127.

The whole platinum boiling apparatus was thoroughly cleaned and rinsed out twice with this acid and all the acid used was poured directly from the bottle into the platinum. At no time during the test was the acid allowed to come into contact with glass after leaving the original bottle.

Some of the acid was boiled about forty-five minutes and the platinum basket containing the gold used in the previous test was soaked in this acid about two hours. About 300 cc. of the acid were boiled in the second platinum dish 45 m., when the platinum basket containing the gold was introduced and the boiling continued. As the joint between the platinum dish and the platinum cover is poor there was necessarily considerable evaporation of the acid and when the gold began to stick out of the acid the boiling was stopped, the gold having been boiled a little less than two hours.

It is estimated that the solution when cold would have been about 130 cc., but the hot solution was diluted a little, poured off from some small pieces of mechanically separated gold and allowed to stand over night. In the morning the cold solution was filtered and the filter caught 0.66 mg. of gold. The filtered solution showed 86.31 mg. of gold or at the rate of over 660 mg. per liter.

The remaining gold is still in use preparing a strong solution with a new lot of acid to be used for some stability tests. On December 27th, 25 cc. of this solution showed 4.94 mg. of gold. On January 27th, there was a slight scum of gold on the surface of the liquid of which 5 cc. showed 4.94 mg. of gold. The final weight amounted to 28.724 grams and contained 3.06 mg. of silver, 0.29 mg. of copper and traces of lead.

As a further test, proof gold, made with great care at the Philadelphia Mint as described by McCaughey,[1] was rolled out very thin and boiled in a conical flask for five hours in previously boiled nitric acid from the freshly opened bottle of Baker's acid mentioned above. The strip exposed about seven square inches of surface to the acid. An accident caused some loss of the dissolved gold, but 11.58 mg. were recovered from the solution.

My personal opinion is that the temperature required to boil 1.42 acid (120°) has fully as much, if not more, to do with dissolving the gold than the strength of acid employed.

The method followed in determining the gold in the strong solutions consisted in evaporating to dryness, digesting gently with a little aqua

[1] THIS JOURNAL, 31, 1262.

regia, adding a liberal amount of strong hydrogen sulphide water, and, after gentle heating, adding some nitrate of silver solution, so that the sulphide of gold would be enclosed and protected by the sulphide of silver. The sulphides were filtered off, put into a porcelain crucible and the filter burned off carefully. The metallic sponge remaining was enclosed in a small cornucopia of sheet lead, more silver added and cupelled.

After trying various methods of gathering a little gold out of a solution containing much silver, I have come to prefer strong hydrogen sulphide water as it is a most excellent precipitant for the gold and the co-precipitated silver protects the gold in the subsequent operations, which are simplified for the sulphide precipitate over a chloride of silver precipitate. In practice a limited amount of the hydrogen sulphide water is added to the solution, which is allowed to stand, with occasional stirring, a day or two, before filtering.

It is a very easy matter to exhibit the solubility of finely divided gold in strong nitric acid. By alloying a small piece of gold with $2^1/_2$–3 times its weight of silver, and dissolving out the silver in diluted nitric acid the gold will be left in good condition for such a test. Five minutes' hard boiling in a few cubic centimeters of strong nitric acid, which may have been previously boiled if desired, will give a distinctly yellow solution, which may be further tested for gold.

The discussion of the application of these results to the question of gold bullion assaying is reserved for a future paper on the general subject of the accuracy of such assaying, but I would say that the practical conclusion of Hillebrand and Allen,[1] that the solubility of the gold in the parting acid in ordinary ore assaying is negligible, is undoubtedly sound, unless the ores be most unusually rich in gold, but the excessive boiling in nitric acid sometimes used by them in their tests might dissolve an appreciable amount of gold in very rich ores and even this drastic treatment is not entirely sure to remove all of the silver, unless more than three parts of silver to one of gold were present originally.

BUREAU OF THE MINT, WASHINGTON, D. C.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

HALIDE BASES OF TANTALUM.

BY WILLIAM H. CHAPIN.

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Preparation of a Lower Bromide of Tantalum from the Pentabromide.

While attempting to produce a lower bromide of tantalum by reduction of the pentabromide in hydrogen, Van Haagen[2] obtained a small

[1] *Loc. cit.*

[2] Thesis, "Tantalum and Some of Its Halides," Univ. of Pa., 1909.